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*Wolcott Gibbs*  
*Osmyl-Nitrate*

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## ON OSMYL-DITETRAMIN.

BY WOLCOTT GIBBS, M. D.,

*Rumford Professor in Harvard University.*

My researches on the metals of the platinum group were interrupted many years since by the want of a laboratory in which the separation and collection of osmic hyperoxide,  $\text{OsO}_4$ , could be effected without serious danger to the air-passages and to the eyes. As I may not be able to take up the subject again, I will here give the results of my study of a peculiar compound of osmium, oxygen, and the elements of ammonia, of much interest from a theoretical point of view.

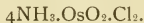
In 1844<sup>1</sup> Frémy described a yellow crystalline substance which he obtained by adding ammoniac chloride to a solution of potassic osmate, and to which he gave the formula,



representing its formation by the equation,



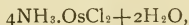
In examining this salt I found that it gave a crystalline compound with platinic chloride, and a further study showed that it yielded by double decomposition with salts of silver a well-defined crystalline sulphate, nitrate and oxalate. I therefore<sup>2</sup> proposed for it the formula,



According to this view the formation of the salt may be represented by the equation,



The subject was taken up some time after by Claus,<sup>3</sup> who ascribed to the chloride the formula,

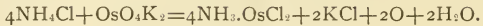


so that it would be the osmium analogue of well-known compounds of palladium, platinum, iridium and ruthenium. If this view be

<sup>1</sup>Annales de Chimie et de Physique, 3d Series, 12, 522.

<sup>2</sup>American Journal of Science, 2d Series, 25, 248. <sup>3</sup>N. Petersb. acad. Bull. 1, 121 and 6, 179.

correct, the formation of the salt would be represented by the equation,

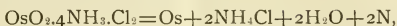


It will be seen that Claus's formula requires that free oxygen should be given off in the formation of the chloride. In repeated preparations I have never found this to be the case. On Claus's view the chloride contains two molecules of water of crystallization. According to all analogy this water should be given off at a temperature below that at which decomposition of the salt itself takes place. To determine this point I heated a portion for an hour to successive temperatures of  $100^\circ$ ,  $115^\circ$ ,  $130^\circ$ ,  $140^\circ$  and  $154^\circ$  C. The total loss after the five hours was 0.59 per cent., the salt being in appearance slightly decomposed. A loss of one molecule of water only would correspond to 4.84 per cent. These facts appear to me to show that the formula which I proposed is correct. Frémy's view would scarcely be defended by any chemist at the present time.

I propose to call the complex  $\text{OsO}_2 \cdot 4\text{NH}_3$ , which we may for the sake of convenience consider as an integral part of each salt in the series, osmyl-ditetramin, to distinguish it from osmio-ditetramin,  $\text{Os} \cdot 4\text{NH}_3$ , which remains to be discovered, and which would correspond to the palladium, platinum, ruthenium and iridium salts above referred to.

*Chloride of Osmyl-ditetramin.* When concentrated solutions of sal-ammoniac and potassic osmate are mixed, an orange-yellow crystalline precipitate of the chloride of osmyl-ditetramin usually separates at once. The potassic osmate should be added in small excess, and the salt after precipitation washed with cold water and dried *in pleno* over sulphuric acid. It is slightly soluble in cold water; hot water readily dissolves but soon decomposes it, with evolution of free osmic hyperoxide,  $\text{OsO}_4$ , and precipitation of a black powder. Strong chlorhydric acid precipitates the chloride from its solutions as a crystalline yellow or orange-yellow powder. The salt may be dissolved in hot water containing a little chlorhydric acid, and gives a deep orange-yellow solution, from which it separates, on cooling, in small deep brown-yellow crystals. The chloride is completely decomposed by ignition, leaving pure metallic osmium as a grey porous mass. It is necessary, however, as Frémy has stated, to ignite in a current of hydrogen to avoid loss

by the formation of osmic hyperoxide. The decomposition by heat is expressed by the equation,



and furnishes perhaps the most simple and convenient method of obtaining pure metallic osmium. To prevent oxidation completely the osmium should be heated to a high temperature, and allowed to become cold in a current of hydrogen, which must afterward be displaced by carbonic dioxide and finally by air. Finely divided osmium oxidizes easily in the air, giving off vapors of osmic hyperoxide. It also exhibits in a remarkable degree the property possessed by spongy platinum, of causing the combination of oxygen and hydrogen, but the osmium is oxidized at the same time. This fact lends some support to the chemical theory of the action of platinum under the same circumstances.

Of the chloride:

0.7850 gram gave 0.4158 gram osmium = 52.96 per cent.

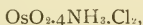
0.9520 gram gave 0.5065 gram osmium = 53.20 per cent.

0.6102 gram gave 80 cc. of nitrogen (moist) at 5° C. and 754.37 mm. = 15.87 per cent.

0.8667 gram gave 0.6813 gram AgCl = 19.45 per cent. chlorine.

1.1565 gram gave 0.3546 gram water = 3.46 per cent. hydrogen.

These analyses agree fairly well with the formula,



which requires:

		Calc'd.	Found.	Calc'd.	
Osmium	199	53.78	53.20 52.96	53.15	194
2 Chlorine	71	19.19	19.45	19.45	71
12 Hydrogen	12	3.24	3.46	3.29	12
4 Nitrogen	56	15.14	15.89	15.34	56
2 Oxygen	32	8.65	...	8.77	32
	370	100.00		100 00	365

The osmium was determined by careful ignition in a current of hydrogen and afterward of carbonic dioxide. To estimate the chlorine, the salt was ignited with sodic carbonate and the reduced osmium separated by filtration.

Nitrogen was determined by Simpson's method, and hydrogen by combustion with oxide of copper. In judging analyses of this and similar compounds, it must be borne in mind that the salt is difficult to purify by repeated crystallization, on account of the

facility with which it is decomposed, and also that the atomic weight of osmium is very uncertain. As will be seen, the analyses agree much better with the formula if we adopt for osmium the atomic weight proposed by Mallet,<sup>1</sup> 194, but I have not considered myself justified in changing the value generally received. Seubert<sup>2</sup> has recently shown that the atomic weights of platinum and iridium are lower than was supposed, and has suggested that the same is true in the case of osmium.

A solution of the chloride of osmyl-ditetramin gives with one of potassic ferro-cyanide a fine violet color. The reaction is very delicate, and affords the best method yet discovered for the detection of minute quantities of osmic hyperoxide in the wet way. In applying this test, the metal must first be oxidized. This may be easily effected by heating the alloy or compound of whatsoever kind in a silver crucible with caustic potash and potassic nitrate and then distilling the fused mass with nitric acid. The distillate is to be rendered alkaline by a small quantity of caustic potash, and then reduced to potassic osmate,  $\text{OsO}_4\text{K}_2$ , by a drop or two of alcohol or of a solution of potassic nitrite. A solution of ammoniac chloride, sulphate or nitrate, is then to be added, after which potassic ferro-cyanide gives a more or less well-defined violet color. In this manner it is possible to recognize quantities of osmium too small to be detected by the characteristic odor of the hyperoxide.

*Chlorplatinate.* This salt is best prepared by boiling the finely pulverized chloride with a solution of platonic chloride. It forms beautiful orange-yellow crystals, slightly soluble in cold water.

Of this salt :

0.4800 gram gave 0.2608 gram osmium and platinum = 54.33 per cent., and 0.1308 gram platinum = 27.25 per cent., giving 0.1300 gram osmium by difference = 27.08 per cent.

The formula  $\text{OsO}_3.4\text{NH}_3.\text{Cl}_2 + \text{PtCl}_4$  requires 27.38 per cent. platinum and 26.82 per cent. osmium. In the analysis of this compound, the weight of the two metals was first obtained by reduction with hydrogen. The osmium was then volatilized by roasting the mixture in a current of oxygen at a red heat.

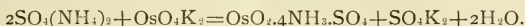
*Sulphate.* The sulphate, like the other salts of the series, is best prepared by pouring a solution of potassic osmate,  $\text{OsO}_4\text{K}_2$ ,

<sup>1</sup>American Journal of Science, 2d Series, 29, 55, 56.

<sup>2</sup>Wiedemann's Annalen, B. 207, 1-50.



into a concentrated cold solution of ammoniac sulphate. Its formation may be represented by the equation,



The sulphate forms beautiful small crystals which have a fine orange-yellow color. It dissolves rather freely in hot, but slightly in cold water.

Of this salt:

0.7580 gram gave 0.3597 gram osmium = 47.45 per cent.

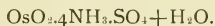
1.7484 gram gave 0.9933 gram  $\text{SO}_4\text{Ba}$  = 23.40 per cent.  $\text{SO}_4$ .

1.2396 gram gave 0.3972 gram water = 3.56 per cent. hydrogen.

0.6490 gram gave 0.2055 gram water = 3.51 per cent.

1.2067 gram gave 138 cc. nitrogen (moist) at 6.5 and 765.80 mm. = 13.99 per cent.

The analyses lead to the formula,



		Calc'd.	Found.	Calc'd.	
1 Osmium	199	47.93	47.45	47.55	194
4 $\text{SO}_4$	96	23.36	23.40	23.53	96
14 Hydrogen	14	3.41	3.51	3.56	14
4 Nitrogen	56	13.62	13.99	13.72	56
3 Oxygen	48	11.68		11.77	48
	413	100.00		100.00	408

*Nitrate.* The nitrate is most easily prepared by pouring a solution of potassic osmate into a cold saturated solution of ammoniac nitrate. The salt separates after a time in granular orange-yellow crystals which are paler in color than those of the sulphate. It is the least stable of the salts which I have examined, the cold solution being soon decomposed with evolution of free osmic hyperoxide.

*Oxalate.* The oxalate is the most stable salt which I have obtained. It is readily prepared by the process given for the other salts, employing of course ammoniac oxalate. The salt separates in beautiful yellow or orange-yellow crystals, which are but slightly soluble in cold water. In this salt:

1.0345 gram gave 0.5133 gram osmium = 49.62 per cent.

1.1553 gram burnt with  $\text{CuO}$  gave 0.3441 gram water = 3.30 per cent. hydrogen and 0.2713 gram  $\text{CO}_2$  = 6.40 per cent. carbon.

1.2817 gram gave 0.3834 gram water = 3.32 per cent. hydrogen.

1.8541 gram gave 234 cc. of nitrogen (moist) at  $12.5^\circ \text{C}$ . and 761.74 mm. = 14.94 per cent.

These analyses correspond tolerably well with the formula,



		Calc'd.	Found.	Calc'd.		
Osmium	199	51.19	49.62	50.78	194	
C <sub>2</sub> O <sub>4</sub>	88	22.86	23.47	23.04	88	
Hydrogen	12	3.11	3.30	3.32	3.14	12
Nitrogen	56	14.54	14.94	14.67	56	
Oxygen	32	8.30		8.37	32	
	<u>387</u>	<u>100.00</u>		<u>100.00</u>	<u>382</u>	

As in the cases of the chloride and sulphate, the analyses correspond better with the assumption that the atomic weight of osmium is 194.

Claus obtained a solution of the oxide or hydroxide of osmyl-ditetramin by digesting a solution of the chloride with argentic oxide. Jacoby first converted the chloride into sulphate by digestion with argentic sulphate, and then decomposed the sulphate with baryta water. The solutions thus obtained are yellow, alkaline, and very easily decomposed.

When a solution of potassic osmate is poured into a cold strong solution of hydrochloride of narcotin, cinchonin or strychnine, a white precipitate is formed in either case which dissolves readily in dilute chlorhydric acid. The solutions give precipitates with platinic and auric chlorides. It seems at least possible that new bases are formed in which the higher alkaloids replace the ammonia of osmyl-ditetramin.

When a solution of potassic osmate is mixed with one of chloride of luteocobalt,  $\text{Co}_2(\text{NH}_3)_{12}\text{Cl}_6$ , a buff-colored precipitate is formed, which on addition of dilute chlorhydric acid becomes orange-yellow and beautifully crystalline. The salt dissolves in cold water without decomposition, but the solution is decomposed on gentle heating. It gives beautiful crystalline salts with auric and platinic chlorides. In the orange-yellow salt:

0.5647 gram gave 0.2642 gram cobalt and osmium = 46.70 per cent.

0.2642 gram of the mixed metals lost 0.2085 gram osmium as  $\text{OsO}_4$  = 36.92 per cent., and gave by difference 0.0557 gram cobalt = 9.78 per cent.

0.4529 gram gave 52.5 cc. nitrogen (moist) at 17° C. and 765.9 = 13.51 per cent.

The ratios are here  $\text{OsCo}_2\text{N}_{12}$ , but further analyses are necessary to determine the constitution of the salt. The chlorides of the other cobaltamines also react with potassic osmate. My experiments in this direction were suggested by the reflection that the salts of the cobaltamines in certain points closely resemble the salts of ammonium.

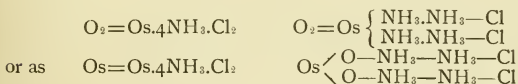
When potassic osmate is mixed with a solution of the chloride of palladio-ditetramin,  $\text{Pd}(\text{4NH}_3)\text{Cl}_2$ , an orange-yellow or sherry wine colored solution is formed. The addition of chlorhydric acid throws down a fine orange-yellow crystalline precipitate. A solution of this salt gives an orange-yellow precipitate with platinum chloride.

The experiments detailed appear to show that interesting results will be obtained by pursuing the subject in the direction which I have pointed out. The very numerous class of metal amines offers a wide field for study.

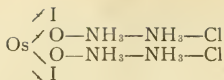
I have also made some observations on other osmium bases which may be mentioned in this connection.

When ammonia is added to a solution of potassic osmate, the liquid immediately takes a sherry-wine color. After addition of an excess of chlorhydric acid and subsequent neutralization with ammonia, the solution gives crystalline precipitates with ammoniac oxalate, auric and mercuric chlorides, etc., and therefore contains a metalamine of some kind. As the osmiamines corresponding to platin-diamin,  $\text{Pt}(\text{NH}_3)_2$ , and platin-ditetramin,  $\text{Pt}(\text{NH}_3)_4$ , have not yet been obtained, it is possible that the base obtained by the action of ammonia upon potassic osmate may represent the osmium analogue of one of these.

The views of Blomstrand as to the constitution of the metalamines have found much favor with chemists, and appear to involve less that is purely hypothetical than any others which have been proposed. Applying this theory to the present case, it will be seen that osmyl-ditetramin chloride may be written either as



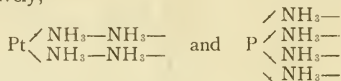
The first view requires us to consider the osmium as tetratomic, while according to the second formula it would be diatomic. If we consider the osmium as diatomic, the chloride ought to form addition products with iodine and bromine, as for instance,



I have sought in vain to form such compounds, and therefore consider the first view as the more probable of the two.

Devillé and Debray<sup>1</sup> have shown that ruthenium forms a hyperoxide the formula of which is  $\text{RuO}_4$ , and which is therefore the analogue of the osmium compound. The close resemblance between the two metals suggests the possibility of forming a ruthenium series similar to that of osmium which I have described, but I have made no experiments to test this suggestion, which I throw out for what it may prove to be worth.

With respect to the nomenclature employed, I may here remark that upon Blomstrand's theory of the constitution of the metal amines, it is possible to distinguish different modes of combination of ammonia by names which are not too cumbrous for ordinary use. Thus we have two series of platinamines which we may write respectively,



In the first platinum is diatomic; in the second tetratomic. If we call the second "platino-tetramin," the first might be termed "platino-ditetramin," and in this manner the difference of atomicity, the number of atoms and the modes of combination of the ammonia are clearly expressed.

The experimental part of the work here published was finished long since. I<sup>2</sup> have delayed its publication in the hope of rendering it more complete, and especially of generalizing the results in various ways, some of which I have indicated above. The work is now given to the public, not as being complete or exhaustive, but simply in the hope that it will be found to contain suggestions which may be of use to other chemists working in the same direction.

CAMBRIDGE, April 15th, 1881.

<sup>1</sup> Comptes Rendus, 83, 926.

<sup>2</sup> The first notice of the true character of Frémy's osmium salt was published jointly by Dr. F. A. Genth and myself (*Am. Jour. Sci. loc. cit.*). Circumstances prevented Dr. Genth from taking any part in the investigation, and I must therefore be held exclusively responsible for all that I have published upon the subject.—W. G.







